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Interaction between poly(vinyl pyridine) and poly(2,6-dimethyl-1,4-phenylene oxide): A copolymer blend miscibility study

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Abstract

The phase behavior of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with random copolymers of styrene and 2-vinyl pyridine, Poly(S-*co*-2VP), as well as with random copolymers of styrene and 4-vinyl pyridine, Poly(S-*co*-4VP), has been investigated in order to estimate the values of the Flory–Huggins parameters $\chi_{\text{PPO,2VP}}$ and $\chi_{\text{PPO,4VP}}$ between PPO and 2-vinyl pyridine, resp. 4-vinyl pyridine. Using previously estimated values for the Flory–Huggins parameters $0.09 < \chi_{\text{S,2VP}} < 0.11$ and $0.30 < \chi_{\text{S,4VP}} < 0.35$, together with the literature value of $\chi_{\text{S,PPO}} = -0.043$, the phase behavior observed as a function of the copolymer composition results in $0.11 \leq \chi_{\text{PPO,2VP}} \leq 0.12$ and $0.46 \leq \chi_{\text{PPO,4VP}} \leq 0.48$. Insight in the interaction between PPO and poly(vinyl pyridine) is of considerable interest for several nanotechnology developments, since PPO is used to improve the mechanical properties of e.g. PS-*block*-P4VP nanorods.

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Keywords: Random copolymer blend; Interaction; Phase behavior

1. Introduction

During the last decades block copolymers have been among the most studied materials not in the least because of their role in almost all aspects of nanotechnology [1–4]. Due to the repulsive forces between the chemically connected blocks, self-assembly into nanoscale structures of a variety of different morphologies occurs [5–11]. These nanostructures can be used for several applications, such as nanoporous membranes [12,13], drug delivery systems [14,15], templates for nano-objects [16–20], etc. Ruokolainen et al. introduced a new concept by hydrogen bonding a phenolic amphiphile such as pentadecylphenol (PDP) to the pyridine groups of poly(styrene-*block*-4-vinyl pyridine), (PS-*b*-P4VP), diblock copolymers. Self-assembly in these systems was shown to give rise the so-called structure-in-structure morphologies, the precise nature depending on the block copolymer composition and the amount of amphiphile added [21–23]. One advantage of this

concept is the fact that after the self-assembling process, the amphiphiles can be easily removed by dialysis, resulting in e.g. polymeric nanoporous materials or core–corona nano-objects [24,25]. Using this procedure, van Zoelen et al. observed that PS-*b*-P4VP nanorods produced via this route had very poor mechanical properties. This is not due to the particular preparation procedure used, but rather results from the lack of entanglements in the PS-core as well as in the P4VP corona. It was shown that this problem can be remedied by adding poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) to the original PS-*b*-P4VP(PDP) system. PPO is miscible with the polystyrene phase only and, in particular because of its low molar mass between entanglements of $M_e = 4200$ g/mol, introduces entanglements in the PS-core already for volume fractions exceeding 0.2 [26]. In this way nanorods with PS/PPO core and P4VP corona were obtained with much improved mechanical properties, which is no surprise knowing the excellent material properties of PS/PPO blends [27].

In the above-mentioned study the PPO homopolymer used has a higher molar mass than the PS-block of the PS-*b*-P4VP diblock copolymer. It is well known that if instead of PPO

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a PS homopolymer had been used, which is chemically identical to the PS-block, the homopolymer would only dissolve in the PS-block domains provided its molar mass is below that of the PS-block [5,28–31]. In the case of PPO the situation is different due to the favorable interaction between PS and PPO [32–36]. This situation has been analyzed theoretically in detail only very recently [37]. One of the conclusions reached is that above a certain minimal amount of PPO, PPO will be present throughout the PS-domains, however, with a parabolic type distribution profile with a maximum near the mid plane and a minimum at the block copolymer interface. For the PS-*b*-P4VP/PPO system all interaction parameters are known except for the interaction between the homopolymer PPO and the P4VP-block. Since this will influence the presence of the PPO at the PS–P4VP interface it is important to have information about its value as well.

Therefore, in this paper we report on our investigation to estimate the value of the Flory–Huggins interaction parameter between PPO and P4VP, as well as PPO and poly(2-vinyl pyridine) (P2VP). To accomplish this, the phase behavior in random copolymer blends of styrene-4-vinyl pyridine P(S-*co*-4VP) and styrene-2-vinyl pyridine P(S-*co*-2VP) with PPO was determined as a function of the copolymer composition.

2. Experimental section

2.1. Materials

Styrene, 4-vinyl pyridine and 2-vinyl pyridine were purchased from Aldrich and were distilled under reduced N₂ pressure and stored at –18 °C before use. 2,2-Azobis(isobutyronitril) (AIBN) was purchased from Fluka and was used as received. Toluene, used as solvent during the polymerization, was freshly distilled from sodium. PPO was purchased from Polymer Source, Inc. and was precipitated from chloroform into methanol and dried under vacuum overnight at 40 °C before use. The characteristics of the PPO samples used are shown in Table 1, in which the subscript denotes the weight average molar mass (kg/mol). The chemical structure of PPO is shown in Fig. 1.

2.2. P(S-*co*-4VP) and P(S-*co*-2VP) synthesis

Copolymers of styrene (S) and 2-vinyl pyridine (2VP) and of styrene and 4-vinyl pyridine (4VP) were synthesized radically using AIBN as initiator (chemical structures are shown in Fig. 1). Several monomer mixtures with different S/2VP or S/4VP ratios (total weight of monomers in between 5 and

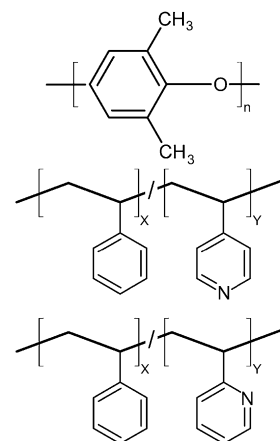


Fig. 1. Chemical structures of the polymers used. From top to bottom: PPO, P(S-*co*-4VP) and P(S-*co*-2VP). For simplicity end groups are not shown.

15 g) were put in ca. 50 ml of toluene in a three-necked round-bottomed flask, equipped with magnetic stirrer, a serum cap and a N₂/vacuum inlet. After degassing using the freeze–thaw method and heating the mixture in an oil bath of 80 °C, an amount of degassed solution of AIBN in toluene (ca. 8 mg/ml) was injected. The amount of initiator solution added corresponded to a desired molecular weight of the polymers of ca. 50,000 g/mol. After ca. 3 h the polymerization was terminated by adding a small amount of hydroquinone in order to prevent the conversion to exceed 10%. The polymers were precipitated twice from toluene into heptane and dried overnight at 40 °C in reduced pressure.

Blends of PPO (50/50 wt.%) and copolymers were made by dissolving equal amounts in chloroform, followed by overnight evaporation of chloroform and drying at 40 °C under reduced pressure.

2.3. Characterization

Elemental analysis was done on a EuroEA3000-CHNS-analyzer to determine the monomer composition in the polymers. A Waters Gel Permeation Chromatograph equipped with two PL-gel mixed-c columns and a refractive index detector was used for determination of the molecular weights, for which dimethylformamide (DMF) with 0.01 M LiBr was used as an eluent. Polystyrene samples were used as calibration standards. Glass transition temperatures were recorded on a DSC Q1000 (TA instruments), at a heating rate of 10 °C/min. In cases where *T_g*s were difficult to observe, modulated temperature scans were performed at a heating rate of 1.0 °C/min and a temperature modulation of 0.5 °C/min. The results are collected in Table 2 for the copolymers with 4-vinyl pyridine and in Table 3 for the copolymers with 2-vinyl pyridine, where the subscript denotes the vinyl pyridine mole fraction in the copolymer.

3. Results and discussion

Blends of two different high molar mass polymers are usually immiscible, because the gain in free energy due to the

Table 1
Characteristics of PPO samples

Sample	<i>M_w</i>	<i>M_n</i>	PDI	<i>N_w</i> ^a	<i>T_g</i> (°C)
PPO _{17.5}	17,500	13,500	1.30	168	208.8
PPO _{35.2}	35,200	25,700	1.37	338	217.3
PPO _{59.8}	59,800	46,000	1.30	574	221.6

^a Calculated on the basis of styrene as segment assuming equal density of all polymers involved.

Table 2
Characteristics of the Poly(S-co-4VP) samples

Sample name	Fraction 4VP (mol%)	M_w (kg/mol)	M_n (kg/mol)	M_v^a (kg/mol)	M_w/M_n	T_g (°C)
PS4VP _{5.7}	5.7	—	—	30.9	—	106.0
PS4VP _{7.1}	7.1	—	—	33.8	—	108.7
PS4VP _{11.8}	11.8	—	—	32.0	—	108.8
PS4VP _{13.9}	13.9	—	—	32.7	—	111.5
PS4VP _{16.8}	16.9	—	—	26.0	—	102.3
PS4VP _{16.9}	16.9	50.2	35.1	—	1.44	106.3
PS4VP _{17.5}	17.5	52.7	37.9	—	1.39	109.7
PS4VP _{20.2}	20.2	50.8	33.6	—	1.51	114.0
PS4VP _{21.4}	21.4	69.2	44.3	—	1.56	111.9
PS4VP _{22.2}	22.2	50.8	33.0	—	1.54	106.7
PS4VP _{39.8}	39.8	63.2	43.0	—	1.47	119.9
PS4VP _{45.7}	45.7	65.0	42.9	—	1.51	125.8
PS4VP _{51.4}	51.4	63.5	42.1	—	1.51	127.0
PS4VP _{56.8}	56.8	64.3	40.1	—	1.60	130.4
PS4VP _{91.7}	91.7	—	—	117.2	—	149.9
PS4VP _{92.2}	92.2	—	—	148.6	—	151.8
PS4VP _{96.5}	96.5	—	—	120.5	—	153.1

^a Characterization of these samples is described in a previous article [41].

increase of entropy is too small to compensate for the unfavorable intermolecular interactions. Miscibility only occurs if these interactions are favorable (often due to intermolecular hydrogen bonding or ionic bonding) or slightly unfavorable. This corresponds to a Flory–Huggins interaction parameter χ which is either negative or very small positive. To determine the value of the χ -parameter between two polymers with a slightly unfavorable interaction, it is sufficient to investigate the miscibility as a function of the respective molar masses and to determine the cross-over between miscible and immiscible. However, this procedure no longer works in the case of strongly unfavorable interactions. In that case it is more convenient to make use of random copolymer blends [38–41]. A most recent example is presented by Winey and co-workers [42] in their paper on the phase behavior of polystyrene and poly(styrene-co-styrenesulfonate). A simple mean-field approach describes the thermodynamic properties of random copolymer blends as a function of the monomer volume fraction in the copolymer. In the case of a monodisperse blend of

a random copolymer $P(A_x\text{-}co\text{-}B_{1-x})$ with a homopolymer $P(C)$, the Gibbs free energy of mixing per segment is given by

$$\frac{\Delta G_m}{nkT} = \frac{\phi}{N_1} \ln \phi + \frac{(1-\phi)}{N_2} \ln (1-\phi) + \chi_{\text{eff}} \phi (1-\phi) \quad (1)$$

where

$$\chi_{\text{eff}} = x\chi_{AC} + (1-x)\chi_{BC} - x(1-x)\chi_{AB} \quad (2)$$

and N_1 , resp. N_2 , denote the chain length of the copolymer, resp. homopolymer, expressed in terms of appropriately selected segments, x denotes the copolymer composition as volume fraction. The components are present in volume fractions ϕ and $(1-\phi)$, respectively. In practical applications we are always dealing with a polydisperse sample in which case the entropic part of Eq. (1) has to be modified to include all different species present. In that case the critical value of χ_{eff} is in a good approximation given by

$$\chi_{\text{eff},c} = 1/2 \left[(N_{w1})^{-1/2} + (N_{w2})^{-1/2} \right]^2 \quad (3)$$

where N_{w1} , resp. N_{w2} , represent the weight average chain length of both blend components involved [43]. In the present study, we are interested in obtaining a value for the Flory–Huggins parameter between poly(4-vinyl pyridine) (P4VP), resp. poly(2-vinyl pyridine) (P2VP), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). This can be realized by investigating random copolymer blends of PPO and P(S-co-4VP), resp. P(S-co-2VP), since $\chi_{S,PPO}$, $\chi_{S,4VP}$ and $\chi_{S,2VP}$ are already known from the literature. For the former a value of $\chi_{S,PPO} = -0.043$ is taken [32,44]. It should, however, be realized that this is only an approximate value and that the real value will, moreover, be temperature dependent. The same is true for the χ -parameter values between PS and P4VP, resp. P2VP. Using copolymer blend studies involving blends of PS with P(S-co-4VP), resp. P(S-co-2VP), these were determined to satisfy $0.30 < \chi_{S,4VP} \leq 0.35$ and $0.09 < \chi_{S,2VP} < 0.11$ [41]. The last result was in excellent agreement with the literature value of $\chi_{S,2VP} = 0.1$ based on various other experiments, thereby lending support to the copolymer blend strategy used. Because 2 out of 3 χ -parameter values are known, the missing values for $\chi_{PPO,4VP}$ and $\chi_{PPO,2VP}$ can be found from miscibility studies on PPO/P($S_x\text{-}co\text{-}4VP_{(1-x)}$) and PPO/P($S_x\text{-}co\text{-}2VP_{(1-x)}$) blends as a function of copolymer composition x .

For the blend studies reported we restricted ourselves to 50/50 wt% blends. Of course, as a consequence of the difference in molar mass between the blend components, in the case of LCST behavior the critical point will usually be located at a slightly different composition. However, in the blend systems investigated we are either dealing with a system that is miscible or immiscible throughout the entire temperature interval studied. For a few homogeneously mixed 50/50 systems that were most relevant to our study, we actually verified that changing the composition did not result in phase separation.

Table 3
Characteristics of the Poly(S-co-2VP) samples

Sample name	Fraction 2VP (mol%)	M_w (kg/mol)	M_n (kg/mol)	M_v^a (kg/mol)	M_w/M_n	T_g (°C)
PS2VP _{5.9}	5.9	—	—	84.6	—	106.0
PS2VP _{8.6}	8.6	—	—	68.6	—	104.5
PS2VP _{11.5}	11.5	—	—	56.7	—	105.4
PS2VP _{16.1}	16.1	—	—	80.9	—	106.2
PS2VP _{16.1}	16.1	—	—	65.1	—	106.0
PS2VP _{17.3}	17.3	—	—	55.1	—	106.0
PS2VP _{46.0}	46.0	62.6	45.9	—	1.36	102.7
PS2VP _{50.4}	50.4	67.5	48.5	—	1.39	101.9
PS2VP _{61.5}	61.5	81.8	52.1	—	1.57	103.9
PS2VP _{70.3}	70.3	84.2	57.0	—	1.48	106.5
PS2VP _{98.8}	98.8	109.7	80.7	—	1.36	126.8
PS2VP _{98.9}	98.9	112.2	80.6	—	1.39	123.4
PS2VP _{99.1}	99.1	124.8	88.2	—	1.41	123.1

^a Characterization of these samples is described in a previous article [41].

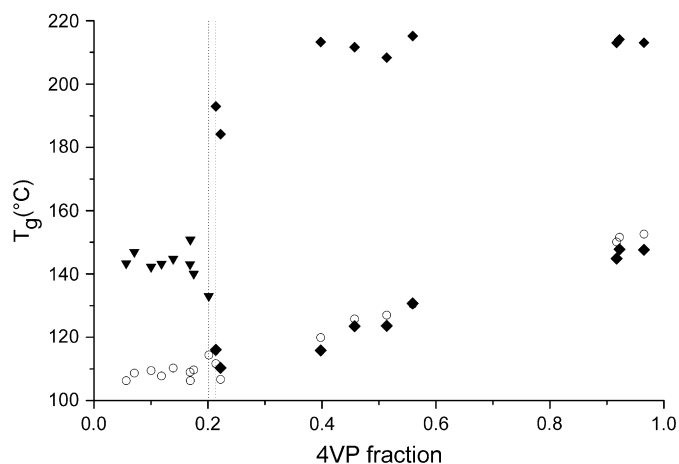


Fig. 2. T_g as a function of the 4VP fraction of P(S-co-4VP). \circ , pure P(S-co-4VP) random copolymers; \blacktriangledown , 50/50 wt% blends of P(S-co-4VP) random copolymers and PPO_{35.2}, resulting in miscible blends with a single T_g . \blacklozenge , 50/50 wt% blends of P(S-co-4VP) random copolymers and PPO_{35.2}, resulting in immiscible blends with 2 T_g s.

In Figs. 2 and 3 the T_g s recorded for both the pure random copolymers as well as the 50/50 wt% blends of P(S-co-4VP) and P(S-co-2VP) with PPO_{35.2} are shown, as a function of the vinyl pyridine fraction in the copolymer. The data presented show that the blends cross-over from being miscible (single T_g) to immiscible (2 T_g s) with increasing vinyl pyridine fraction. In the miscible blends the glass transition temperature is in between that of the components involved, i.e. in between the T_g of PPO and that of the random copolymers. Beyond a critical amount of vinyl pyridine macrophase separation occurs and 2 T_g s approaching the T_g s of the pure components of the blends are observed. It is obvious that the miscibility/immiscibility transition occurs for a considerably larger vinyl pyridine fraction for the 2VP pyridine samples than for the 4VP samples.

Although these data already allow us to derive an approximate value for the χ -parameters, it is possible to investigate

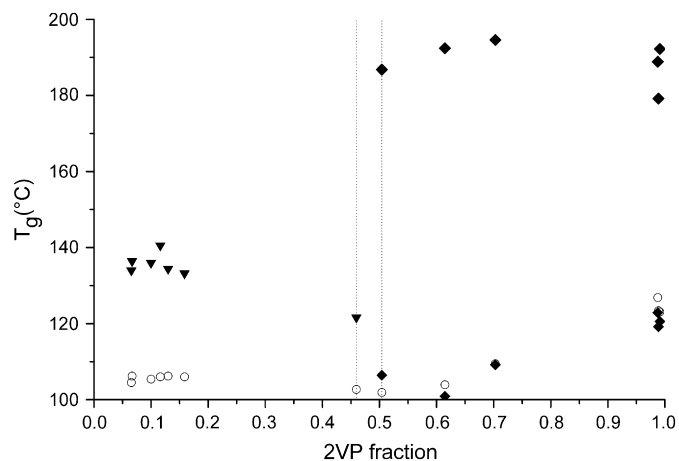


Fig. 3. T_g as a function of the 2VP fraction of P(S-co-2VP). \circ , pure P(S-co-2VP) random copolymers; \blacktriangledown , 50/50 wt% blends of P(S-co-2VP) random copolymers and PPO_{35.2}, resulting in miscible blends with a single T_g . \blacklozenge , 50/50 wt% blends of P(S-co-2VP) random copolymers and PPO_{35.2}, resulting in immiscible blends with 2 T_g s.

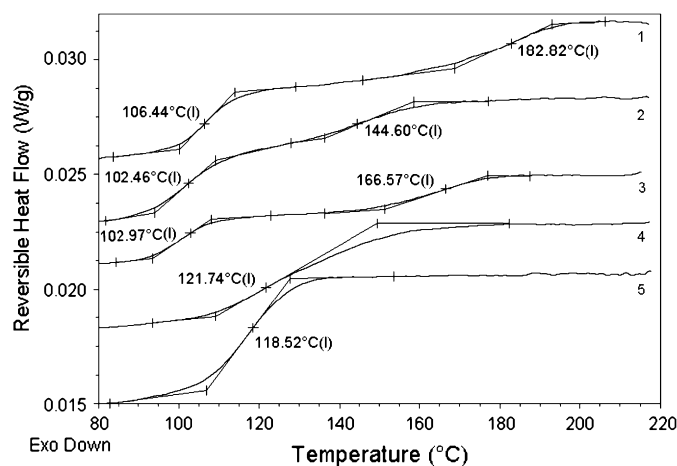


Fig. 4. Reversible heat flow curves of 50/50 wt% blends of P(S-co-2VP) and PPO. (1) PS2VP_{50.4}/PPO_{35.2}; (2) PS2VP_{50.4}/PPO_{17.5}; (3) PS2VP_{46.0}/PPO_{59.8}; (4) PS2VP_{46.0}/PPO_{35.2}; (5) PS2VP_{46.0}/PPO_{17.5}.

the miscible–immiscible cross-over in a little bit more detail by varying the molar mass of PPO. Figs. 4 and 5 show the DSC data for blends involving PPO with three different molar masses (see Table 1 for characteristic properties). Fig. 4 shows that the PS2VP_{46.0}/PPO_{17.5} blend exhibits a single sharp T_g , whereas PS2VP_{46.0}/PPO_{59.8}, involving the highest molar mass PPO, clearly has two T_g s. For the intermediate molar mass PPE the PS2VP_{46.0}/PPO_{35.2} blend has a very broad T_g , indicating that this system is really very close to the cross-over between miscible and immiscible. Furthermore, starting from an immiscible blend with the intermediate molar mass PPO, PS2VP_{50.4}/PPO_{35.2}, we notice that for the lower molar mass PPO_{17.5} the gap between the 2 T_g s, although still present, is strongly reduced. A high temperature LCST could not be observed in any of the blend systems studied. These results are collected in Table 4 together with the lower and upper limits for $\chi_{\text{PPO,2VP}}$ that follow from these observations.

$$0.11 < \chi_{\text{PPO,2VP}} < 0.12 \quad (4)$$

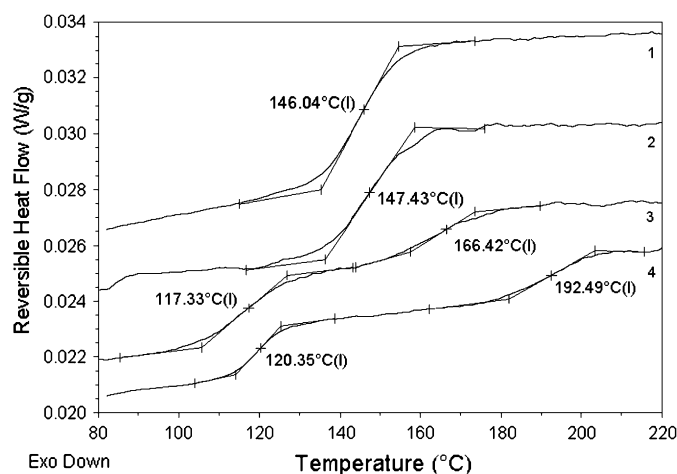


Fig. 5. Reversible heat flow curves of 50/50 wt% blends of P(S-co-4VP) and PPO. (1) PS4VP_{20.2}/PPO_{35.2}; (2) PS4VP_{20.2}/PPO_{59.8}; (3) PS4VP_{21.4}/PPO_{17.5}; (4) PS4VP_{21.4}/PPO_{35.2}.

Table 4
Lower and upper limits for the Flory–Huggins parameter $\chi_{\text{PPO},2\text{VP}}$

Blend	2VP (mol%)	$N_{\text{w},\text{SVP}}^a$	$N_{\text{w},\text{PPE}}^a$	State	$\chi_{\text{PPO},2\text{VP}}$
PS2VP _{50.4} /PPO _{17.5}	50.4	463	168	Immiscible	>0.11
PS2VP _{46.0} /PPO _{59.8}	46.0	438	575	Immiscible	>0.11
PS2VP _{46.0} /PPO _{35.2}	46.0	438	338	Miscible	<0.12

^a Calculated on the basis of styrene as segment assuming equal density of all polymers involved.

Likewise, Fig. 5 shows characteristic DSC thermograms of the most relevant P(S-co-4VP)/PPO blends. The top and bottom curves correspond to PS4VP_{20.2}/PPO_{35.2} and PS4VP_{21.4}/PPO_{35.2}, respectively, and represent a miscible and immiscible system. From these observations it follows that the Flory–Huggins parameter satisfies

$$0.46 < \chi_{\text{PPO},4\text{VP}} < 0.48 \quad (5)$$

When considering these blends with a different molar mass PPO, i.e. PS4VP_{20.2}/PPO_{59.8} and PS4VP_{21.4}/PPO_{17.5}, Fig. 5 demonstrates that the former is still a miscible and the latter an immiscible system, albeit that in the latter case the gap between the two blend T_g s is reduced. These two observations can only be reconciled with if we take a value of $\chi_{\text{S},4\text{VP}}$ close to the upper limit, i.e. $\chi_{\text{S},4\text{VP}} \cong 0.35$. Using this value we then find $\chi_{\text{PPO},4\text{VP}} \cong 0.47$ is in agreement with inequality Eq. (5). Given the simplified nature of the mean-field analysis used and the uncertainty in the values of the other χ -parameter values involved, it is very satisfying that a consistent description of the phase behavior of so many different blends can actually be achieved. As a final remark, we note that if a slightly more negative value is used for $\chi_{\text{S},\text{PPO}}$, as sometimes suggested in the literature, the phase behavior observed results in slightly larger values for $\chi_{\text{PPO},4\text{VP}}$ and $\chi_{\text{PPO},2\text{VP}}$ (Table 5).

Table 5
Lower and upper limits for the Flory–Huggins parameter $\chi_{\text{PPO},4\text{VP}}$

Blend	4VP (mol%)	$N_{\text{w},\text{SVP}}^a$	$N_{\text{w},\text{PPE}}^a$	State	$\chi_{\text{PPO},4\text{VP}}$
PS4VP _{21.4} /PPO _{17.5}	21.4	424	168	Immiscible	>0.46
PS4VP _{20.2} /PPO _{59.8}	20.2	384	575	Miscible	<0.48

^a Calculated on the basis of styrene as segment assuming equal density of all polymers involved.

4. Concluding remarks

In recent years we used PPO to improve the mechanical properties of PS-*block*-P4VP nanorods that were produced via the so-called comb-shaped supramolecules route. If PPO is added in the process, nanorods are obtained consisting of a core containing the PS blocks and the PPO homopolymer and a corona consisting of the P4VP blocks. The PPO will be distributed throughout the PS phase and not mix with the P4VP blocks. Already due to conformational entropy reasons alone, the concentration of PPO will have its minimal value at the PS–P4VP interface. The fact that the interaction between

P4VP and PPO is even more unfavorable than between P4VP and PS implies a small additional suppression of PPO near the interface.

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